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Persistence Study on Gasoline Compound in Soil Matrix and Its Application in Fire Investigation

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Abstract

Adsorptivity of gasoline attached on soil matrix was discussed. Peak areas' changing trend of target compounds' and typical compounds of gasoline were proposed, by fitting peak areas and time. Results shown that retention times of different compounds in gasoline attached on soil were different. C5 alkylbenzene, Naphthalene and Methylnaphthalene had the longest retention time, next come indane and C4 alkylbenzene. C1、C2 and C3 alkylbenzenes have the shortest retention time.

Keywords: gasoline, GC-MS, volatility, fire investigation

1. Introduction

The cost of arson fires to society in the UK has now reached over £1.3 billion a year and it is estimated that arson attacks result in insurance claims of around £550 million per year [1]. Between 2002 and 2004 arson suspected fires caused 316 lives were lost and 9345 people were injured, and each year 20000-30000 homes and businesses are affected by arson [2]. In 2005, 31500 arsons suspected fires caused $664 million dollars in damage to private and public property in the Unites States. In addition to property, 315 lives were lost and over 2000 people were injured [3]. The fire creates not only huge economic loss but also heavy casualties. So, investigation of fire reason is becoming more important. Intentionally set fire is often started by the use of accelerants such as petrol, diesel、paraffin、 kerosene、 paint thinner and lighter fluid, all of which consist of mixtures of volatile organic compounds (VOCs). In many cases petroleum based flammable liquids are a main choice for arsonists because of the low cost and availability. One of the major objectives in the investigation of any suspected arson is the isolation and identification of residual accelerants from the fire residue.

A number of studies have researched the backgrounds produced by different unburnt matrix, such as carpet, shoes, clothes, wood etc. Lentini et al. [4] researched the volatile components detectable in many common objects, ranging from household products to shoes, clothes and carpet. They concluded that carpet samples can contain a number of compounds found in petrol. The aforementioned research by Bertsch [5] also indicated that unburnt carpet can produce discernible levels of petroleum-type hydrocarbons. K. Cavanagh et al. [6] have confirmed that carpet removed from motor vehicles in the general population can exhibit some of the compounds that are diagnostic for petrol residues. However, in the majority of cases, the chromatographic patterns produced by these components can be easily distinguished from those produced by petrol.

Few persistence studies, however, been performed researched the evaporation rate of petrol from various materials. A study by Folkman et al. [7] discovered that petrol was detectable on shoes after a period of 48 h, and on carpet after 7 days.

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The carpet in that study was left in an outdoors environment, at temperatures ranging from 5 to 15℃. K. Cavanagh et al. [6] have a persistence study that was conducted to determine the evaporation and persistence of unleaded petrol on carpet. The results indicated that small volumes of petrol (less than 100 ml) are unlikely to be detected on carpet after a 24 h period. Larger volumes will be detected after this period, but will generally not be detectable after 1 week. A new procedure is presented by Dan Muller et al. [8] for the detection of gasoline on the hands of a suspect. The results indicated that the effectiveness of activated charcoal strip (ACS) for detecting gasoline on a suspect's palm when the Dichloromethane (DCM) as extracting solvent. Even 3 h after a small quantity of gasoline comes into contact with hands of a suspect, it has been possible to detect the presence of this ignitable liquid with the proposed procedure.

In this paper, persistence of gasoline on soil matrix is studied. The volumes of gasoline added are 0.5 ml, and the samples are left for periods ranging from 1 h to 96h. GC-MS is used to determine the chromatographic profile at various stages of evaporation. Compounds frequently found in gasoline are selected, such as toluene, p-xylene, m-xylene, o-xylene and 1, 3, 5 – trimethylbenzene, etc, to analyze the peak areas' changing trend of target compounds' and typical compounds of gasoline.

2. Materials and methods

2.1 Materials and instruments

Table 1.The information of materials and instruments as following:

Name	Company
Gasoline	Chinese National Petroleum Corp (CNPC) in Guangzhou
Hexane	Honeywell
Dichloromethane	Aladdin Chemistry Co. Ltd
Soil	Sun yat-sen university
Agilent GC-MS 7890A-5975C	Agilent Technologies, Inc (USA)

2.2 Sample preparation

The crude soil (200.00g) is sieved by 20 meshes after dried at 120℃ for 10h. 80.0g sieved soil is purified by Soxhlet Extractor with 60ml dichloromethane at 60℃for 10h. Then the soil is heated in a muffle furnace at 250℃ for 2h and heated at 400℃for 2.5h. After that soil is removed to room till the temperature returned to room temperature and is saved in the dryer for use.

6 soil samples are prepared (20g of each sample) and numbered $1^{\#}$-$6^{\#}$ then $2^{\#}$-$6^{\#}$ samples are added 0.5 ml of gasoline and $1^{\#}$ sample is taken as blank-control. All samples are kept indoors in separate rooms and the temperature range from 17.0℃ to 22.0℃, the humidity range from 30% to 70% and no wind. The samples are left for periods 1h、6h、12h、24h and 96h then elution process carried out. The samples are placed in a sealed jar and with 30ml of hexane ultrasonic extraction for 5min and then quantitative concentration to 1 ml. The extract is then transferred to a labelled auto-sampler vial for analysis by GC-MS.

2.3 GC-MS and AMDIS analysis

Analyses are performed on a GC-MS system (Agilent GC-MS 7890A-5975C, USA) under the following instrumental conditions (Table 2). Table 3 shows the Automatic Mass Spectral Deconvolution and Identification System (AMDIS) parameters.

Table 2. The GC-MS conditions as following:

Column	HP-5MS(30m×0.25mm×0.25um)
Split injection	10:1
Temperature program	40℃ (hold 2 min)
	40 - 150℃at 8℃/min (hold 2 min)
	150 - 250℃ at 10℃/min (hold 2 min)
Carrier gas	Helium

Column flow	1.0 ml/min
Sample injection volume	1 ul
Injector temperature	250°C
Transfer line temperature	250°C
Energy of impact	70 eV
MS interface temperature	280 °C
MS ion source temperature	150 °C

The detector is set to scan mode (30-350 m/z) between 3min and 30 min.

Table 3. The AMDIS parameters as following:

Type of analysis	Simple
Minimum match factor	60
Data file format	Agilent files
Instrument type	Quadrupole
Threshold value	Low
m/z	Auto

3. Results and discussion

3.1 Total ion chromatogram of fresh gasoline

Fig 1 shows that the total ion chromatogram (TIC) of fresh gasoline. Chromatogram exhibit the majority of the target compounds of fresh gasoline, such as the C7 - C12 alkanes (Octane, Nonane, Dodecanoic, etc), aromatic hydrocarbon (Toluene, Ethylbenzene, M-xylene, P-xylene and O-xylene, 1-ethyl-3-methylbenzene, 1-ethyl-4-methylbenzene, 1, 3, 5-trimethylbenzene, etc), naphthalene and its isomers, indan and its isomers, etc. In addition, there is a small amount of unsaturated hydrocarbons. The total ion chromatogram (TIC) presented hundreds of organics.

Chromatogram integral result shows that the content of each component is as following: aromatic hydrocarbons(86.779%), alkanes (8.928%), naphthalene(including its isomers) and indan (including its isomers) (2.939%), unsaturated hydrocarbons (1.354%).

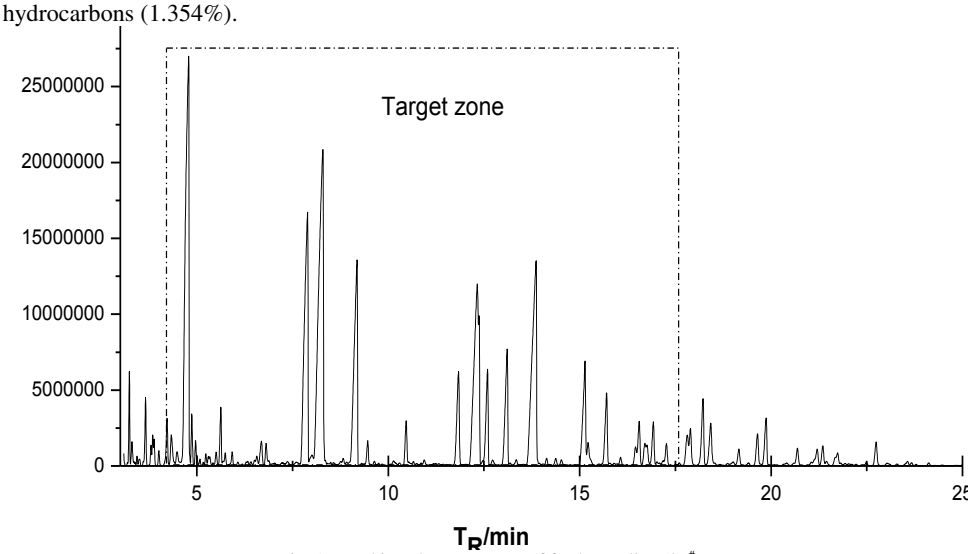


Fig. 1. Total ion chromatogram of fresh gasoline (97#)

Fig 2 indicates that the change of integral area of target compounds with varying lengths of exposure period in target zone (retention time range from 4.0min to 17.5min). The results indicate that integral area of target compounds is decreasing with the extension of exposure time and by the end of the longest exposure period (96h), no compounds present

in chromatographic profile could actually be identified. Based on a line model analysis between total ion chromatographic peak area (Area) and exposure period (Time), the equation (1) is calculated as following:

$$\ln(Area) = 18.3 - 1.41\ln(Time) \quad (1)$$

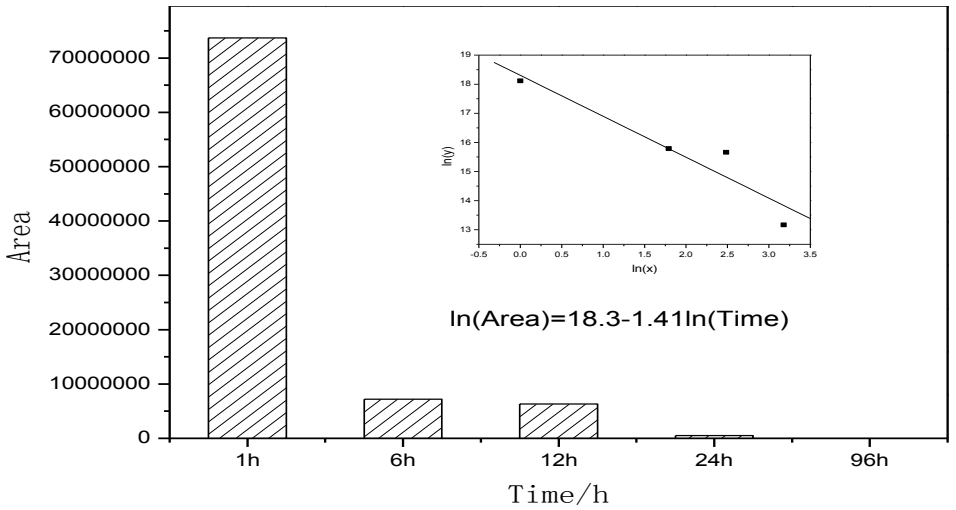


Fig. 2. Relationship between target compounds' peak areas of gasoline and exposure period in soil substrate material

3.2 AMDIS analysis

The free software package AMDIS is widely used for deconvolution of GC–MS data. Some chromatographic peak partially or completely overlay and their mass spectrogram cross of each other because they own similar structures so that interference spectrum library retrieval. In order to obtain the pure mass spectra and its detail chromatographic information, AMDIS is used for analyzing the GC-MS data. This information is compared with target substance's spectral library, chromatographic peak that matching factor value is greater than user setting value is presented.

Table 4 shows information of residue compounds of gasoline after different exposure period (1h, 6h, 12h, 24h, 96h). These compounds are retrieved from self-built spectral library（97GASOLINE.MSL）. The detail information in table 4 indicated that alkanes of gasoline, such as C1, C2 and C3 and C4-alkylbenzene, volatilize firstly. Only C5-alkylbenzene is presented after 24h. Indan and its isomers not be presented when exposure 24h under experimental conditions but naphthalene's isomers are presented. There is no target compounds presented when exposure 96h under experimental conditions. Persistence of the target compounds in soil substrate material is related to both the adsorption effect of soil and the nature of the target compounds, such as boiling point and saturated vapor pressure. Some target compounds' boiling point and saturated vapor pressure are as following: toluene (110.8℃，4kPa/26．03℃), indan (178℃, 9.33kPa/98℃）, naphthalene (218℃, 0.11kPa/50．0℃）. The compound the more easily volatilize under both conditions of higher saturated vapor pressure and lower boiling point. According to above results, the fire investigators should select different target compounds according to the different exposure period, because there are different target compounds present after different exposure period.

Table 4. Information for compounds of gasoline after different exposure period

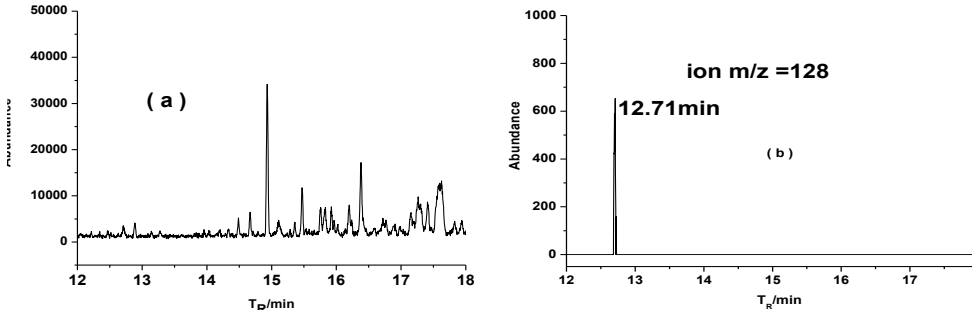
Number	T_R（min）	Name	1h	6h	12h	24h	96h
1	4.19	Toluene	+	-	-	-	-
2	6.05	Ethylbenzene	+	-	-	-	-
3	6.22	P-xylene	+	-	-	-	-
4	6.84	Nonane	+	-	-	-	-
5	8.02	Propylbenzene	+	-	-	-	

6	8.19	1, 2, 3 - trimethyl benzene	+	-	-	-	-
7	8.87	1, 2, 4 - trimethyl benzene	+	+	-	-	-
8	8.96	Decane	+	-	-	-	-
9	9.75	Indan	+	-	-	-	-
10	9.93	Indene	+	-	-	-	-
11	10.05	1 - methyl - 4 - propyl benzene	+	+	+	-	-
12	10.21	2, 4 - dimethyl - 1 - ethyl benzene	+	-	-	-	-
13	10.67	1 - methyl indan	+	-	-		-
14	10.98	Undecane	+	+	+	-	-
15	11.17	1, 4 - dimethyl - 2 - ethyl benzene	+	-	-	-	-
16	11.45	1, 2, 3, 4 - methyl benzene	+	+	+	-	-
17	11.82	4 - methyl indene	+	+	+	-	-
18	12.70	Naphthalene	+	+	+	-	-
19	12.88	Dodecane	+	+	-	-	-
20	14.43	Pentamethylbenzene	+	+	+	+	-
21	14.70	2 - methyl naphthalene	+	+	+	+	-
22	16.93	2, 7 - dimethyl naphthalene	+	+	+	+	-

+ found compound and – not found compound

3.3 Extracted ion chromatograms analysis

Fig 3(a) shows the total ion chromatogram after 96h period（retention time from 12.00min to 18.00min）. No target compounds are found by chromatogram analysis and AMDIS retrieval in target zone. Fig 3(b)-3(d) show the extracted ion chromatograms. Naphthalene (m/z128), methyl naphthalene (m/z142) and dimethyl naphthalene (m/z156) are selected as extracted ion to analyze the extracted ion chromatograms profiled. Fig 3(b)-(d) indicate the presence of extracted ion chromatogram of m/z=128 (at 12.71 min), m/z = 142(at 14.70min) and m/z = 156(at 16.90 min). This result indicates the presence of naphthalene, methylnaphthalene, and dimethyl naphthalene. Analyze the residual compounds of gasoline by extracting ion chromatograms combined with the retention time.



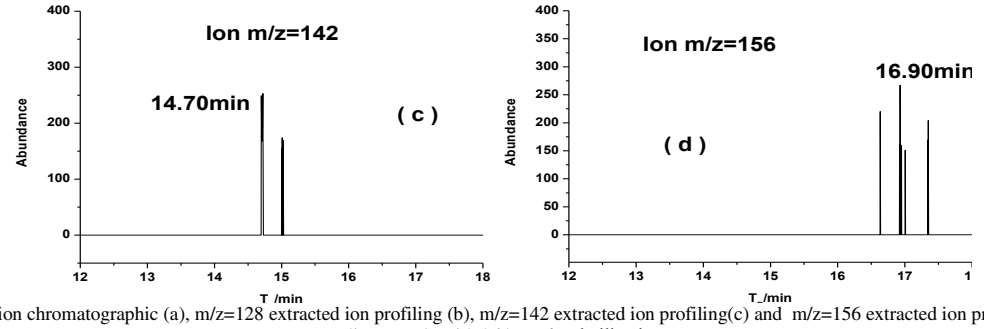


Fig. 3. Total ion chromatographic (a), m/z=128 extracted ion profiling (b), m/z=142 extracted ion profiling(c) and m/z=156 extracted ion profiling(d) of gasoline sample with 96 hours' volatilization.

4. Conclusion

Persistence of gasoline on soil substrate material is studied in this paper. Peak areas' changing trend of target compounds and typical compounds of gasoline are obtained by fitting peak areas and time. Results shown that persistence times of different compounds in gasoline attached on soil are different. C5-alkylbenzene, Naphthalene and Methylnaphthalene had the longest persistence time, next come indane and C4-alkylbenzene. C1、C2 and C3-alkylbenzenes have the shortest persistence time. These data provide the reference for fire investigators when they analyze the presence of gasoline or not. This study only studied the persistence of gasoline on the soil substrate material. For arson cases, gasoline often attached on clothes, skin, hair, etc. So, the persistence of gasoline research on clothes, skin, hair, etc that is necessity for future research.

Acknowledgments

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